

SIMPLIFIED METHOD FOR OBTAINED STRONG ADHESIVE BONDING OF COMPOSITES TO DENTIN, ENAMEL AND OTHER SUBSTRATES

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This application is a continuation-in-part of co-pending application Ser. No. 699,079, filed Feb. 7, 1985, which is in turn a continuation-in-part of co-pending application Ser. No. 516,956, filed July 25, 1983, now U.S. Pat. No. 4,521,550, which is in turn a continuation-in-part of co-pending application Ser. No. 457,029, filed Jan. 10, 1983, now U.S. Pat. No. 4,514,527.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to simplified methods of improving adhesive bonding of acrylic resins to industrial, natural, and dental substrates, and more particularly to dental restoration methods and methods of improving adhesion of composite dental materials to dentin and enamel. More specifically, methods for strong adhesive bonding of composite resins to dentin and enamel are disclosed with the objects of improving treatment of cervical erosions, root caries, potential dental decay, fractures, and other dental conditions and of eliminating much mechanical cutting of dentin and enamel now required for retention of restorations. The complete disclosures of U.S. Pat. No. 4,514,527 and U.S. Pat. No. 4,521,550 and allowed U.S. patent application Ser. No. 699,079, filed Feb. 7, 1985, are expressly incorporated herein by reference.

2. Description of the Prior Art

For many years, advances in the study of methods of adhesive bonding of composite materials to hard tooth tissues have evolved by small increments. Previous experiments in adhesive bonding of composite materials to dentin demonstrated beneficial effects from cleansers, mordants, and adhesion promoting coupling agents; see, for example, Bowen, R. L., "Adhesive Bonding of Various Materials to Hard Tooth Tissues. XXII. The Effects of a Cleanser, Mordant, and PolySAC on Adhesion Between a Composite Resin and Dentin," 59 *J. Dent. Res.* 809-814 (1980); Bowen, R. L., "Use of Polyfunctional Surface-Active Comonomer and Other Agents to Improve Adhesion Between a Resin or Composite Material and a Substrate," U.S. Pat. No. 4,251,565, February 1981; Bowen, R. L., "Adhesive Bonding of Various Materials to Hard Tooth Tissues. XIX. Solubility of Dentinal Smear Layer in Dilute Acid Buffers," 28 *Int'l Dent. J.* 97-104 (1978); Bowen, R. L., "Adhesive Bonding of Various Materials to Hard Tooth Tissues. VII. Metal Salts as Mordants for Coupling Agents," in Moskowitz, H.; Ward, G.; & Woolridge, E., (eds.); *Dental Adhesive Materials* 205-221, Proceedings from Symposium held Nov. 8-9, 1973 at the Hunter-Bellevue School for Nursing, New York City, Prestige Graphic Services (1974).

The rationale for using a surface-active comonomer as a coupling agent to improve bonding has been supported by previous data. Bowen, R. L., "Adhesive Bonding of Various Materials to Hard Tooth Tissues. II. Bonding to Dentin Promoted by a Surface-Active Comonomer," 44 *J. Dent. Res.* 895-902 (1965); Bowen, R. L., "Adhesive Bonding of Various Materials to Hard

Tooth Tissues. III. Bonding to Dentin Improved by Pretreatment and the Use of a Surface-Active Comonomer," 44 *J. Dent. Res.* 903-905 (1965); Bowen, R. L., "Adhesive Bonding of Various Materials to Hard Tooth Tissues. IV. Bonding to Dentin, Enamel, and Fluorapatite Improved by the Use of a Surface-Active Comonomer," 44 *J. Dent. Res.* 906-911 (1965); Bowen, R. L., "Adhesive Bonding of Various Materials to Hard Tooth Tissues V. The Effect of a Surface-Active Comonomer on Adhesion to Diverse Substrates," 44 *J. Dent. Res.* 1369-1373 (1965). The addition reaction product of N-phenylglycine and glycidyl methacrylate (NPG-GMA) and the addition reaction product of N-phenylglycine and p-chlorophenyl glycidyl ether (NPG-CGE) are disclosed, respectively, as vehicles to improve adhesive bonding to a limited extent in Bowen, U.S. Pat. No. 3,200,142, Aug. 10, 1965, and in Bowen, British Pat. No. 1,448,134 and U.S. Pat. No. 3,785,832, Jan. 15, 1974.

Although an acid-etch technique has been effective in benefiting the bonding of composite and unfilled resins to enamel of teeth, no method has existed for achieving strong adhesive bonding between composite and unfilled resins and dentin. Many investigators have been attempting to achieve significantly enhanced adhesive bonds to both dentin and enamel and various other substrates for well over twenty-five years without adequate success.

SUMMARY OF THE INVENTION

The present invention comprises alternative materials and simplified methods which give strong adhesive bonds between composite materials or resins and dentin and also result in effective bonding between these materials or resins and enamel and other natural or industrial substrates with greater color stability of the resultant materials than previously achieved. Thus, it is an advantage of this invention to provide better material and methods that make it easier to obtain aesthetic adhesive bonding of composite and unfilled resins of the type polymerized by free radicals to dentin, enamel, industrial substrates, and/or other substrates containing or capable of binding metallic ions (i.e., ions of elements on the left side and in the center of the periodic table). The resulting products are also within the scope of the invention.

Briefly, the simplified method of the invention is preferably accomplished by a two-step technique which comprises first treating the surface to be bonded with an acidic solution preferably containing nitric or other strong acid, polyvalent cations, and compounds such as oxalic acid or other polyfunctional acids which can form relatively water-insoluble precipitates with calcium and other polyvalent cations at pH values above that of the acidic aqueous treatment solution, and also containing at least one compound selected from the group consisting of (1) N-phenylglycine ("NPG"), (2) the adduct of N(p-tolyl)glycine and glycidyl methacrylate ("NTG-GMA"), (3) the addition reaction product of N-phenylglycine and glycidyl methacrylate ("NPG-GMA"), and (4) other amino acids. Secondly, a solution is applied which contains at least one monomeric compound selected from the group consisting of (1) the addition reaction product of pyromellitic acid dianhydride and 2-hydroxyethyl methacrylate ("PMDM"), (2) the addition reaction product of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 2-hydrox-